

Magnetic properties in the doped spin-1/2 honeycomb-lattice compound $\text{In}_3\text{Cu}_2\text{VO}_9$

Y. J. Yan¹, Z. Y. Li¹, T. Zhang¹, X. G. Luo¹, G. J. Ye¹, Z. J. Xiang¹, P. Cheng¹, Liang-Jian Zou² and X. H. Chen^{1*}

¹ Hefei National Laboratory for Physical Science at Microscale and Department of Physics,
University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China and

² Institute of Solid State Physics, Chinese Academy of Sciences,
Hefei, Anhui 230031, People's Republic of China

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We report the magnetic properties in the Co- and Zn-doped spin-1/2 honeycomb-lattice compound $\text{In}_3\text{Cu}_2\text{VO}_9$. The magnetic susceptibility and specific heat experiments show no long-range ordering down to 2 K in $\text{In}_3\text{Cu}_2\text{VO}_9$. In the low temperature range, approximately T^2 -dependent magnetic specific heat and linearly T -dependent spin susceptibility were observed, suggesting a spin liquid candidate with a $S = 1/2$ honeycomb lattice. When Cu^{2+} ions are partially substituted by Co^{2+} ions, both impurity potential scattering and magnetic impurity scattering induced by magnetic Co^{2+} ions break the homogenous spin-singlet spin liquid state, and lead to an antiferromagnetic (AFM) long-range correlation. While replacing Cu^{2+} with nonmagnetic Zn^{2+} ions, the frustration and antiferromagnetic correlation between Cu^{2+} ions is weakened, leading to breakage of a spin liquid state and suppression of the low-dimensional AFM.

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I. INTRODUCTION

Dimensionality and the spin magnitude S play important roles in the physical properties of interacting systems because the quantum fluctuation is affected significantly by them. The quantum fluctuation enhanced both by geometric frustration and by spin frustration may destroy the antiferromagnets (AFM) order and yield a rich variety of ground states, novel excitations and exotic behaviors that currently attract much attention. The magnetic properties of a solid reflect the arrangement of the magnetic ions in its crystal structure. Low-dimensional antiferromagnets exhibit a variety of ground states depending on the spin number and the spin configuration [1]. In the first few years following the discovery of high temperature superconductivity by Bednorz and Möller [2], $S=1/2$ 2D systems on a square lattice have been in the center of attention. Since the discovery of the honeycomb-lattice Heisenberg antiferromagnet (AF) $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$, it revealed a novel spin-liquid-like behavior down to low temperature which is ascribed to the frustration effect due to the competition between the AF nearest- and next-nearest-neighbor interactions J_1 and J_2 [3–5], growing interest arises in the low-dimensional magnets with honeycomb lattice. The honeycomb lattice is a loosely-coupled lattice with the number of the nearest-neighbor sites only three, it might be susceptible to the fluctuation effect caused by frustration, and its ordering property is of special interest. Experimentally there are only a few examples of materials where the electron spins are located in a two-dimensional honeycomb lattice. However, diverse phenomena, such as spin-glass state [6, 7], spin-liquid state [3], Kosterlitz-Thouless transitions [8, 9], or

superconductivity [10, 11], have been reported.

Recently, a complex transition metal oxide, $\text{In}_3\text{Cu}_2\text{VO}_9$, was suggested as a possible candidate for the realization of the $S=1/2$ honeycomb lattice [12]. $\text{In}_3\text{Cu}_2\text{VO}_9$ was previously reported to crystallize in the hexagonal space-group $P6_3/mmc$, consisting of alternating layers of $[\text{InO}_6]$ octahedra, and Cu^{2+} and V^{5+} ions in a trigonal-bipyramidal coordination [12]. The Cu^{2+} ($3d^9$, $S=1/2$) ions were proposed to be arranged in a 2D network of hexagons with the nonmagnetic V^{5+} ($3d^0$) ions in the center of each hexagon. A later structural neutron diffraction study revealed that a structural $\{\text{V1Cu6}/3\}$ order in the hexagonal planes has a finite correlation length $\xi_{st} \sim 300 \text{ \AA}$ and that these structural domains are randomly arranged along the c axis [13]. The static susceptibility $\chi(T)$ shows a broad maximum at $T_0 \sim 180 \text{ K}$, being a characteristic feature of a low-dimensional antiferromagnet, and passes through a kink at $T_1 \sim 38 \text{ K}$ followed by a peak at $T_2 \sim 28 \text{ K}$. The anomaly at T_2 previously identified with the transition to the long range ordered state [12] have been tentatively assigned to glass-like order of unsaturated spins in domain boundaries by Möller *et al.* [13]. The real origin of the peak-like anomaly is under debate.

To obtain insights into the nature of the puzzle properties of spin liquid, especially the ground state of $\text{In}_3\text{Cu}_2\text{VO}_9$, we have investigated the magnetic properties of the Co- and Zn-doped spin-1/2 honeycomb-lattice compound $\text{In}_3\text{Cu}_2\text{VO}_9$. We show that the T -dependent magnetic susceptibility and specific heat in undoped $\text{In}_3\text{Cu}_2\text{VO}_9$ resemble to that of a spin liquid. When the Cu^{2+} ions are partially substituted by Co^{2+} ions, the low-dimensional antiferromagnetism (AFM) at 180 K is quickly killed, while a long-range AFM transition can be observed in the temperature range from 50 K to 80 K, depending on Co concentration. When doping Zn into the Cu sites, the low-dimensional AFM and the

*Corresponding author; Electronic address: chenxh@ustc.edu.cn

anomaly at T_2 in the magnetic susceptibility are gradually suppressed, and completely disappear with heavily Zn doping level.

II. MATERIAL PREPARATION AND METHODS

$\text{In}_3\text{Cu}_2\text{VO}_9$ polycrystalline pellets were synthesized by a conventional solid-state technique. The starting materials, In_2O_3 , CuO , and V_2O_5 in a molar ratio of 3:4:1 were thoroughly ground and pressed into pellets. They were then heated at 1173 K in air for five days with several intermediate grindings and pelleting. $\text{In}_3\text{Cu}_{2-x}\text{Co}_x\text{VO}_9$ or $\text{In}_3\text{Cu}_{2-x}\text{Zn}_x\text{VO}_9$ was synthesized using In_2O_3 , CuO , V_2O_5 , Co_3O_4 or ZnO as starting materials. The raw materials were accurately weighed according to the stoichiometric ratio of the chemical formulas, and then synthesized using the similar procedure to $\text{In}_3\text{Cu}_2\text{VO}_9$.

The samples were characterized by X-Ray diffraction (XRD) using Rigaku D/max-A X-Ray diffractometer with $\text{Cu K}\alpha$ radiation in the range of 10° - 70° with the step of 0.02° at room temperature. Sample purity was checked by powder x-ray diffraction, which showed no impurity peaks except for the sample $\text{In}_3\text{Cu}_{1.5}\text{Co}_{0.5}\text{VO}_9$ in which the trace of In_2O_3 is observed. Magnetic susceptibility was measured using Vibrating Sample Magnetometer (VSM). Specific-heat measurements were carried out from 2 K to room temperature using Quantum Design Physical Property Measurement System (PPMS).

III. RESULTS AND DISCUSSION

Fig.1(a) and (b) show the powder x-ray diffraction patterns for $\text{In}_3\text{Cu}_{2-x}\text{Co}_x\text{VO}_9$ and $\text{In}_3\text{Cu}_{2-x}\text{Zn}_x\text{VO}_9$ polycrystalline samples, respectively. It is found that all the peaks in XRD diffraction pattern can be well indexed to a hexagonal structure. As seen in the inset of Fig. 1(a), when Co doping concentration is less than 0.1, the lattice parameters for a- and c-direction decrease firstly, reach minima at $x=0.04$, and then increase with further Co doping. When Co doping concentration is more than 0.1, the lattice parameter of a-direction decreases monotonously with increasing Co doping concentration while that of c-direction increases monotonously. In the $\text{In}_3\text{Cu}_{2-x}\text{Zn}_x\text{VO}_9$ system, the lattice parameter for c-direction increases with Zn doping concentration, while the change of the lattice parameter for a-direction is not obvious.

The static magnetic susceptibility $\chi(T)$ for $\text{In}_3\text{Cu}_2\text{VO}_9$ was measured in a magnetic field of 1 T. The temperature dependence of χ for $\text{In}_3\text{Cu}_2\text{VO}_9$ reveals a broad maximum at $T_0 \sim 180$ K, being a characteristic feature of a low-dimensional antiferromagnet, and passes through a kink at $T_1 \sim 38$ K followed by a peak at $T_2 \sim 28$ K and shows a Curie-like upturn at lower temperatures (as seen in the inset of Fig. 2 (a)). Temperature dependence of

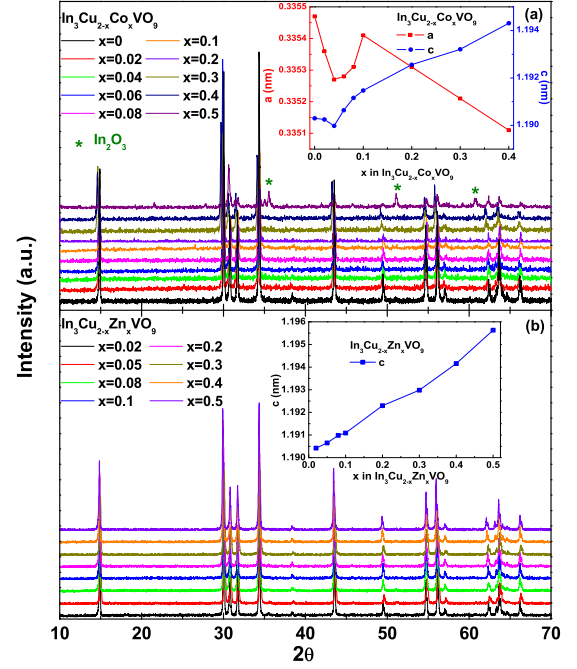


FIG. 1: (Color online) Powder x-ray diffraction patterns at room temperature for polycrystalline samples, (a): $\text{In}_3\text{Cu}_{2-x}\text{Co}_x\text{VO}_9$, (b): $\text{In}_3\text{Cu}_{2-x}\text{Zn}_x\text{VO}_9$. The peaks marked with stars reveal the existence of the impurity phase In_2O_3 . Insets are doping dependence of a and c-axis lattice parameters.

specific heat divided by T for $\text{In}_3\text{Cu}_2\text{VO}_9$ is shown in the inset of Fig. 2 (b), no signature for a magnetic transition above 2 K has been observed. These results are consistent with the previous reports[13–15]. Since the experimental data of both the specific heat and magnetic susceptibility do not exhibit long-range AFM ordering, one naturally assumed that the ground state of $\text{In}_3\text{Cu}_2\text{VO}_9$ might be a gapless spin liquid phase, and a long-time searched exotic quantum phase is performed both in theory and in experiment. In Fig. 2, the spin susceptibility of Cu^{2+} ions is obtained using the similar method as described in Ref. 12 (details given in Ref. 16). A nearly T -linear dependence of χ_M can be observed by fitting the data between 2 K and 16 K as is seen in Fig. 2 (a). The magnetic specific heat of Cu^{2+} ions below 30 K is obtained by subtracting the phonon contributions (details given in Ref. 17), which is shown in Fig. 2(b). Several features have to be mentioned: (i) C_M shows nearly no field dependence with $\mu_0 H \leq 9$ T, and it is common in spin liquid candidates [18]. This behavior has also been observed for other spin liquid candidates, such as NiGa_2S_4 with Ni^{2+} ($S=1$) triangular lattice [19] and $\text{Na}_4\text{Ir}_3\text{O}_8$ with Ir^{4+} ($S=1/2$) hyperkagome lattice [20]. (ii) with the log-log scale, between 2 and 7.5 K, C_M can be fit as $C_M = bT^\alpha$ with $b = 1.29 \text{ mJ K}^{-3} \text{ mol}^{-1}$ and $\alpha = 2.39$. (iii) C_M shows a broad hump around 17 K. According to the early study [21], a gapless spin liquid phase in Kagome lattice may demon-

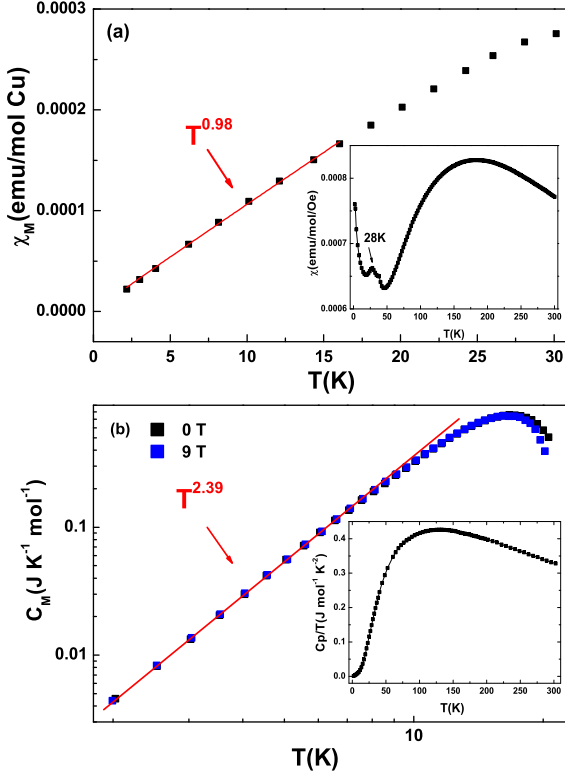


FIG. 2: (Color online)(a): Temperature dependence of spin susceptibility of Cu^{2+} ions in $\text{In}_3\text{Cu}_2\text{VO}_9$ parent compound below 30 K under 1 T. The inset of Fig.2(a) shows the static magnetic susceptibility of $\text{In}_3\text{Cu}_2\text{VO}_9$ in the temperature range from 2 K to 300 K under 1 T. (b): Temperature dependence of magnetic specific heat C_M of Cu^{2+} ions. The inset of Fig.2(b) shows temperature dependence of specific heat divided by T for $\text{In}_3\text{Cu}_2\text{VO}_9$. The red solid lines are fitting curve as described in the text.

strate unusual temperature dependence behavior in the low-T range: the specific heat is T^2 -dependent, and the magnetic susceptibility linearly increases with increasing temperature. Therefore, we find that our experimental data on the T-dependent magnetic specific heat and spin susceptibility almost obey these predictions for a spin liquid state in a kagome lattice, in addition to small deviations which are attributed to the contributions from magnetic impurities and fitting error. It indicates that the ground state of $\text{In}_3\text{Cu}_2\text{VO}_9$ might be a spin liquid phase.

Theoretically, Sondhi *et al.* [22] showed that in a honeycomb Heisenberg model, when the next-nearest-neighbour spin coupling is larger than 0.08 times and smaller than 0.3 times of the nearest-neighbour spin coupling, strong spin frustration and spin fluctuations can stabilize a spin liquid phase in a Heisenberg insulator. $\text{In}_3\text{Cu}_2\text{VO}_9$ is a charge transfer insulator with the energy gap of 1.6 eV, which is confirmed by the GGA+U simulation done by Gou *et al.*[23]. Well localized magnetic moments in honeycomb copper spins with $S=1/2$

form a hexagonal net in the Cu-V-O layer, showing that the low-energy magnetic properties of $\text{In}_3\text{Cu}_2\text{VO}_9$ can be described by a honeycomb Heisenberg model. In this material, though the direct next-nearest-neighbour (NNN) spin coupling between copper spins is small, the indirect next-nearest-neighbour can not be negligible. On the one hand, the Cu-Cu superexchange coupling via oxygen ions can contribute a fraction of NNN interaction; on the other hand, wide V 3d bands and its hybridization with coppers may contribute another fraction of NNN superexchange coupling. Hence, the NNN spin coupling and spin fluctuation [12] may play important role to drive the system from the Néel AFM ground state to the spin liquid one.

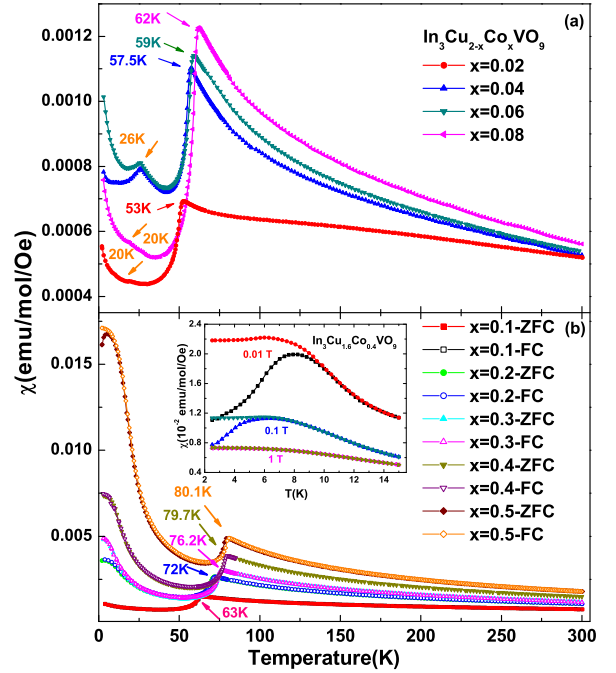


FIG. 3: (Color online) Temperature dependence of magnetic susceptibility for $\text{In}_3\text{Cu}_{2-x}\text{Co}_x\text{VO}_9$ polycrystalline samples in the temperature range from 2 K to 300 K under 1 T. Arrows denote the occurrence temperature of the long range AFM ordering and the peak-like anomaly. The inset shows the magnetic susceptibility of $\text{In}_3\text{Cu}_{1.6}\text{Co}_{0.4}\text{VO}_9$ at low temperature under various fields.

Temperature dependence of the static magnetic susceptibility for the $\text{In}_3\text{Cu}_{2-x}\text{Co}_x\text{VO}_9$ samples is shown in Fig.3 (a) and (b). The Weiss temperature is positive which is obtained by fitting the magnetic susceptibility between 200 K and 300 K to the Curie-Weiss law $\chi = C/(T-\theta) + \chi_0$ (C is curie constant, θ is the Weiss temperature, and χ_0 is the temperature-independent term), indicating an antiferromagnetic interaction between divalent transition metal ions (TM^{2+}). The effective magnetic moment of the transition ions TM^{2+} increases from $1.29 \mu_B$ for $\text{In}_3\text{Cu}_{1.96}\text{Co}_{0.04}\text{VO}_9$ to $2.32 \mu_B$ for $\text{In}_3\text{Cu}_{1.6}\text{Co}_{0.4}\text{VO}_9$. The spin number of Co^{2+} ions is $3/2$.

When the Cu^{2+} ions are partially substituted by Co^{2+} ions, the low-dimensional antiferromagnetism (AFM) at about 180 K is quickly destroyed, while a long-range AFM transition can be observed in the temperature range from 50 K to 80 K (marked by arrows in Fig. 3), depending on Co concentration. The transition temperature T_N of the long-range AFM order increases with Co concentration, tends a finite temperature of about 80 K when x is large than 0.4. Meanwhile, one notes that the magnitude of the magnetization increases with increasing Co concentration due to the larger intrinsic magnetic moment of Co^{2+} than Cu^{2+} . When the Co doping level is less than 0.08, there is a peak-like anomaly with a curie-like upturn below 40 K. The anomaly is suppressed and disappears when Co doping level is more than 0.08. As shown in Fig. 3(b), a trace of spin glasslike contribution with $T_g < 10\text{K}$ is observed. The difference between zero-field cooling and field cooling magnetization is suppressed with increasing field, and becomes negligibly small at high fields above 1 T, as seen in the inset of Fig. 3(b). This behavior is similar to that observed in the hyperkagome lattice $\text{Na}_4\text{Ir}_3\text{O}_8$ [20].

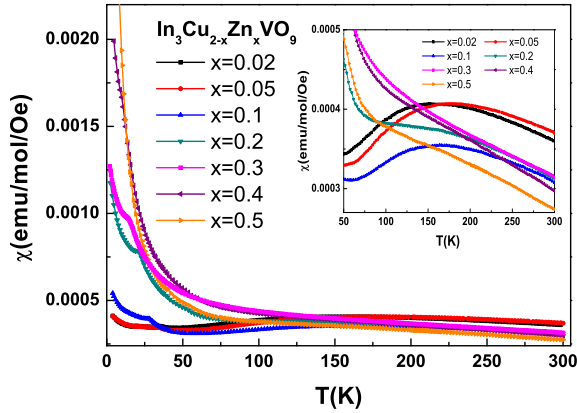


FIG. 4: (Color online) Temperature dependence of magnetic susceptibility for $\text{In}_3\text{Cu}_{2-x}\text{Zn}_x\text{VO}_9$ polycrystalline samples in the temperature range from 2 K to 300 K under 1 T. The inset shows enlarged magnetic susceptibility $\chi(T)$ above 50 K.

In order to compare with Co doping, we tried to dope non-magnetic Zn^{2+} ions into Cu^{2+} sites. Fig. 4 shows the temperature dependence of static magnetic susceptibility of the $\text{In}_3\text{Cu}_{2-x}\text{Zn}_x\text{VO}_9$ samples. By replacing Cu^{2+} with Zn^{2+} ions, both the intensity and the temperature of the peak-like anomaly are suppressed with increasing Zn concentration, and the anomaly is killed when Zn concentration is more than 0.3. As seen in the inset of Fig. 4, the broad hump at T_0 is notable when Zn concentration x is less than 0.2, and tends to be suppressed with higher Zn doping, and disappears when $x \geq 0.3$. The Weiss temperature and effective magnetic moment for $x=0.3, 0.4, 0.5$ samples are 19.6 K, 2.3 K, 1.2 K and $0.30 \mu_B, 0.29 \mu_B, 0.26 \mu_B$, respectively. They are much

smaller than that of Co-doped samples. Therefore, with increasing Zn^{2+} doping concentration, the frustration is suppressed gradually, and the antiferromagnetic correlation strength between Cu^{2+} ions is weakened, leading to the breakage of a spin liquid state and suppression of the low-dimensional AFM. Once $x \geq 0.3$, the strength of the correlation between Cu^{2+} ions is not large enough to form antiferromagnetic order, and a paramagnetic state is observed.

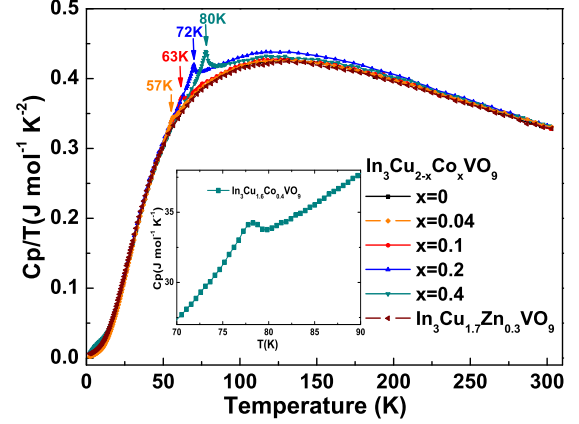


FIG. 5: (Color online) Temperature dependence of specific heat divided by T for the samples of $\text{In}_3\text{Cu}_{2-x}\text{Co}_x\text{VO}_9$ and $\text{In}_3\text{Cu}_{2-x}\text{Zn}_x\text{VO}_9$ systems. The inset shows the anomaly in specific heat for $\text{In}_3\text{Cu}_{1.6}\text{Co}_{0.4}\text{VO}_9$ around the phase transition.

Fig. 5 shows the specific heat divided by T for partial samples of these two systems. A λ -shape-like jump is observed in all the Co-doped samples ranging from 50 K to 80 K, which is ascribed to long range AFM transition. For $\text{In}_3\text{Cu}_{1.7}\text{Zn}_{0.3}\text{VO}_9$ without low-dimensional AFM behavior, no anomaly is observed around the temperature corresponding to the peak at about T_2 of the magnetic susceptibility. Therefore, the peak-like anomaly of the magnetic susceptibility is not associated with long-range ordering. It is inconsistent with the results reported by Yehia et al. [15], they claimed that strong experimental evidence for the formation of the Néel type collinear AFM spin structure was found in the $S=1/2$ honeycomb plane at temperatures below ~ 20 K. In contrast, a neutron diffraction study revealed that a structural $\{\text{V1Cu6/3}\}$ order in the hexagonal planes has a finite correlation length $\xi_{st} \sim 300 \text{ \AA}$ and these structural domains are randomly arranged along the c axis [13]. The peak-like anomalies have been tentatively assigned to glass-like order of unsaturated spins in domain boundaries by Möller et al. [13]. Therefore, we consider the peak-like anomaly of magnetic susceptibility is not associated with long-range ordering, and might arise from unsaturated spins in domain boundaries.

After substituting Cu^{2+} with Co^{2+} in $\text{In}_3\text{Cu}_2\text{VO}_9$, one expects that the location of Co^{2+} ions is random. Ob-

viously, both impurity potential scattering and magnetic impurity scattering induced by Co^{2+} ions ($S = 3/2$) break the homogenous spin-singlet spin liquid state, releasing the AFM long-range correlation and leading to the AFM behaviors in specific heat and magnetic susceptibility. Such a scenario can address various T-dependent properties over wide doping range we observed in experiments, for example the various AFM-paramagnetic (PM) phase transition peak as observed in specific heat and magnetic susceptibility in many doped samples. The antiferromagnetic correlation length of magnetic TM^{2+} ions increases with increasing Co^{2+} concentration, leading to higher AFM transition temperature. Meanwhile, by replacing Cu^{2+} with nonmagnetic Zn^{2+} ions which is also random located, the antiferromagnetic correlation between Cu^{2+} ions is destroyed, breaking the homogenous spin-singlet spin liquid state and suppression of the low-dimensional AFM.

IV. CONCLUSION

In summary, we successfully synthesized Co- and Zn-doped spin-1/2 honeycomb-lattice compound $\text{In}_3\text{Cu}_{2-x}\text{Co}_x\text{VO}_9$ ($0 \leq x \leq 0.5$) and $\text{In}_3\text{Cu}_{2-x}\text{Zn}_x\text{VO}_9$

($0 \leq x \leq 0.5$), and studied their magnetic properties. The magnetic susceptibility and specific heat experiments of $\text{In}_3\text{Cu}_2\text{VO}_9$ show no long-range ordering down to 2 K. Approximately T^2 -dependent magnetic specific heat and linearly T-dependent spin susceptibility in the low temperature range were observed in $\text{In}_3\text{Cu}_2\text{VO}_9$, suggesting a spin liquid candidate with a $S = 1/2$ honeycomb lattice. When the Cu^{2+} ions are partially substituted by Co^{2+} ions, the low-dimensional antiferromagnetism (AFM) at about 180 K is quickly destroyed, while a long-range AFM transition is observed in the temperature range from 50 K to 80 K, depending on Co concentration. Both impurity potential scattering and magnetic impurity scattering induced by magnetic Co^{2+} ions break the homogenous spin-singlet spin liquid state, releasing the AFM long-range correlation. While replacing Cu^{2+} with nonmagnetic Zn^{2+} ions, the frustration and antiferromagnetic correlation between Cu^{2+} ions is weakened, leading to breakage of a spin liquid state and suppression of the low-dimensional AFM.

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